

# Hydrogen generation under electrolysis process using Ni diffusion catalytic membranes as electrodes

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**Abstract:** The work presents a setup scheme for studying the processes of hydrogen generation and analysis of its penetration through diffusion-catalytic membranes directly during the electrolysis process, as well as first experimental results obtained when testing this setup (volt-ampere characteristics, mass spectra of the mixtures of gases, generated during electrolysis, etc.).

**Key-Words:** Electrolysis, nickel, diffusion catalytic membrane, hydrogen generation, mass-spectrum.

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## 1 Introduction

In work [1] in order to obtain especially pure hydrogen under the electrolysis process, it was proposed to use special cathode designs. For instance, it could be beneficial to use membranes in the form of nickel tubes or other metals with high hydrogen permeability, like palladium and its alloys. In this case, one end of the cathode (diffusion-catalytic membrane) is hermetically sealed by argon-arc welding, and the other one is connected through a valve to a vacuum volume or to a hydrogen accumulator, e.g. similar as it was used in works [2-3], for production of extra pure hydrogen in the flame of combustion of hydrocarbons. Such a device would be able to provide the possibility to obtain ultra-pure hydrogen (with a purity of more than 99.999% vol.) through the electrolysis along with the production of technical hydrogen or a combustible mixture (explosive gas, Brown's gas). To prove the scientific concept for such technology realisation, special installation was created and experimentally tested. Presented below first results experiments confirm the potential advantages of such approach aiming at generation of pure hydrogen to be used in various applications.

## 2 Experimental and Results

A schematic diagram of the experimental setup is shown in Fig. 1. Experimental installation consists of two chambers by 1 dm<sup>3</sup> volume of each that made of thick-walled stainless steel 12Cr18Ni10Ti. One of them is served as electrolysis chamber (1) and the other is used for measurements (2). In the first chamber, a diffusion-catalytic membrane made of Ni-99.95 (4(1)) is placed through a fluoroplastic seal-insulator (3). It forms a tube with the diameter of 5.5 mm, the thickness of 0.2 mm and overall length of 400 mm, which is hermetically sealed by argon-arc welding at one end. Opposite end of the tube 4(1) is connected through the valve (5) to the vacuum volume of chamber (2) for measuring the pure hydrogen flow. Chamber (2) provides the technical ability to place various samples for studying the hydrogen permeability, including in-situ measurements under conditions of exposure to glow discharge plasma. For temperature measurements inside the membranes, a chromel-copel thermocouple (9) has been installed. The pressure in the electrolysis chamber (1) and the vacuum in chamber (2) are measured by pressure gauge (10) and thermocouple gauge PMT-2 (8) respectively. An electric potential can be supplied to

both membranes: in chamber (1) for electrolysis process, and in chamber (2) for igniting a glow discharge. This design of the experimental installation allows not only studying the processes during electrolysis and the hydrogen permeability of diffusion-catalytic membranes, but also allows investigations on the possibility of decomposition of water vapour and electrolysis products under the plasma discharge conditions.

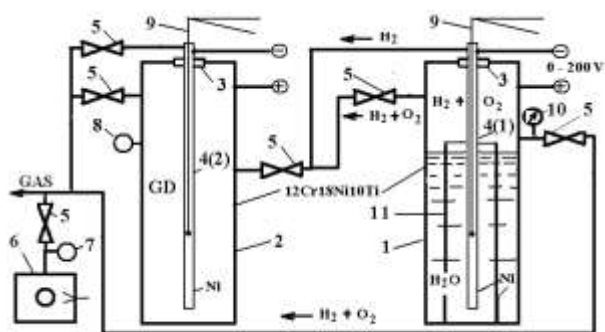


Fig.1. Scheme of the experimental electrolysis installation: 1 – electrolysis chamber (E-1); 2- measuring (plasma) chamber; 3- insulators; 4(1) and 4(2) – Ni membranes; 5 – valves; 6 – fore vacuum pump 2PVR-5D; 7, 8 – vacuum gauges PMT-2; 9- chromel-copel thermocouples; 10 - pressure gauge; 11 – replaceable anode.

The electrolysis chamber (E-1) is connected through a valve (not shown in the diagram) to the inlet system of the high-vacuum installation GAS (Fig. 2), which allows, using the mass – spectrometry to determine the composition of the mixture of gases formed during the electrolysis process [4,5]. Hydrogen is produced by electrolysis in following way. At first, the internal volumes of the membrane 4(1), the measuring chamber (2) and the connecting pipes were pumped out to the pressure of about  $10^{-3}$  Torr. This pressure is measured by vacuum gauge (8) and it is considered as initial pressure  $P_0$ . Then the electrolysis process is started in chamber (1), shown in Fig. 1, by switching on a constant voltage between anode and cathode. The voltage source (0-200V) was a rectifier with four D132-80 diodes connected through a current-limiting resistor. The electrolyte used was 1% solution of  $\text{NaHCO}_3$  (soda) in filtered tap water. Mineralization measured using a TDS Meter-3 device has achieved 140 ppm. The current-voltage characteristic of the electrolysis process is presented in Fig.3. The temperature of the electrolyte (cathode) increases monotonically over time, reaching  $50^\circ\text{C}$  after half hour of operation of the electrolysis chamber (Fig. 4).

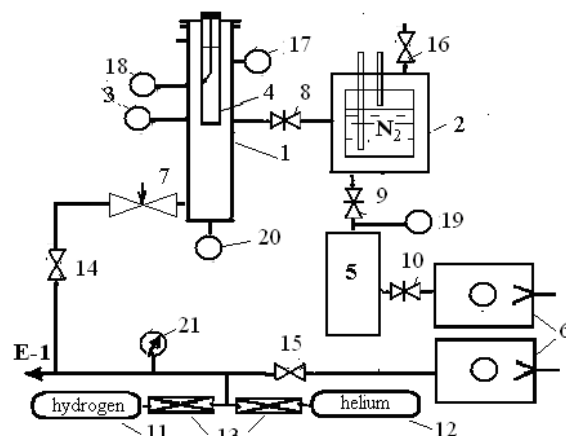


Fig.2. Scheme of the GAS experimental setup: 1 - vacuum chamber; 2- cryogenic pump; 3- mass spectrometer MX-7304; 4- sample; 5- diffusion pump M-500; 6 - fore-vacuum pumps 3NVR-1D; 7- fine adjustment valve; 8, 9, 10 - high-vacuum valves; 11-hydrogen balloon, 12-helium balloon; 13 - gas reducers; 14, 15, 16 - high pressure valves; 17 – ionization gauge PMI-10; , 18, 19 – thermocouple gauges PMT-2; 20 – ionization gauge PMI-2; 21- pressure gauge.

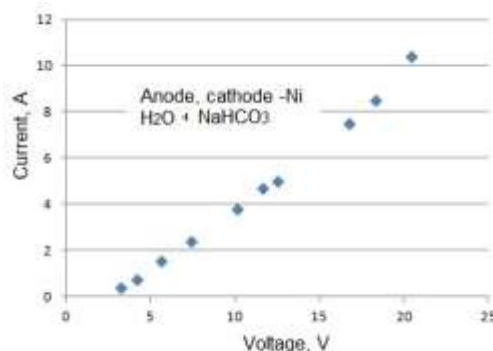


Fig.3. Current-voltage characteristic at electrolysis of a solution of soda in water (1 wt.%).

At the same time, the current increases up to 4.3-4.6A, and the voltage between the electrodes decreases from 10V to - 7.3V. Gas pressure in electrolysis chamber reached 4 atmospheres (free volume in electrolysis chamber is about  $0.5 \text{ dm}^3$ , so we have  $\sim 2 \text{ dm}^3$  of gas at the normal conditions). It is quite enough to carry out precise measurements of mass-spectra.

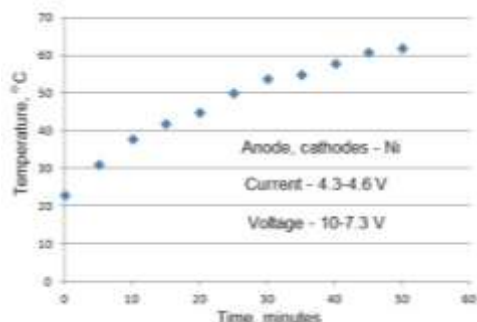


Fig.4. Dependence of the membrane temperature on the time of electrolysis

To determine the composition of the gas mixture, formed during electrolysis, vacuum chamber (1) of the GAS installation was pumped out to a pressure of  $1 \cdot 10^{-6}$  Torr. Through the valve 5 (Fig. 1), and through valves 14, 7 (Fig. 2) the gas, generated during the electrolysis process, has been released into vacuum chamber (1) of the GAS device to a pressure of  $0.1 \cdot 10^{-4}$  Torr. The mass spectra measured with MX-7304 mass spectrometer and recorded, using the WAD-AIK-BUS analogue module and a computer. Figure 5 (a, b) shows the obtained spectra before and during the puffing of gas generated under electrolysis into the vacuum chamber. In this case, the pressure in the electrolysis chamber was about 4 atm, and the electrolyte temperature was  $\approx 45^\circ\text{C}$ . For comparison, the spectrum is shown in Fig. 5c when pure hydrogen (99.99% by vol.) is injected from a balloon.

The next experiment was carried out to test the device in regime of pure hydrogen generation. The hydrogen flow through a diffusion-catalytic nickel membrane has been measured by following procedure. Hydrogen, which is formed on the Ni-membrane surface facing to the electrolyte, absorbs, diffuses through the membrane volume, and then desorbs to the internal volume of the membrane. Only hydrogen is able pass through the diffusion-catalytic nickel membrane, which separates the hydrogen from other gases with larger mass. Thus, the generated hydrogen, as confirmed by our measurements, has a high purity – better than 99.999 % vol. As soon as hydrogen desorbs, the pressure P in the vacuum chamber (2) increases. The measurements of hydrogen flow through Ni membrane (productivity) were carried out with the method of constant pressure, similar to the described previously [6, 7].

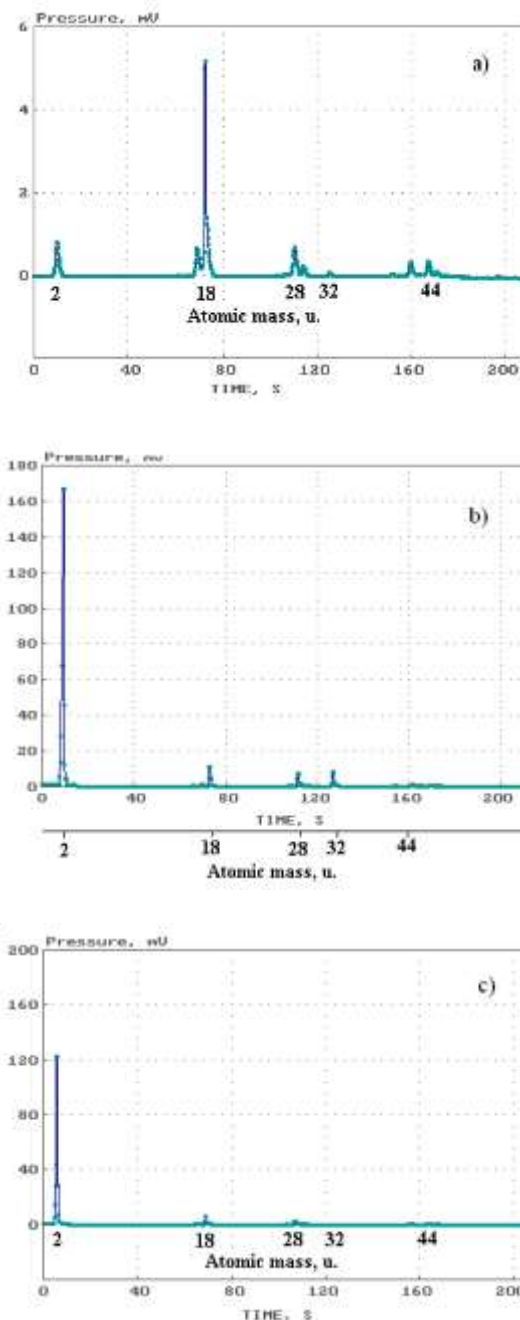


Fig.5. Mass spectrum of gases in the GAS chamber: (a) before inlet, (b) during inlet of gas from the electrolysis chamber (E-1); (c) hydrogen puffing from hydrogen balloon.

The hydrogen flow Q in our case corresponds to the hydrogen amount generated per time unit. If the membrane surface area is taken into account, one possible to obtain the specific hydrogen flow – hydrogen amount generated per time unit from membrane surface area unit. We used the following units: normal  $\text{cm}^3$  ( $\text{cm}^3$  of gas at the atmosphere pressure and at the room temperature) of hydrogen per second ( $\text{Ncm}^3/\text{s}$ ) or liters of hydrogen gas at the

atmosphere pressure per hour (l/hour). The specific hydrogen flow  $q(\text{N}\cdot\text{cm}^3/\text{s}\cdot\text{cm}^2)=Q/F$ , where  $F$  is the membrane work surface area (faced to electrolyte), was used, too. For technical reasons, the cathode temperature not monitored in this experiment, but the temperature of the chamber wall, measured by a thermocouple, was  $\sim 170^\circ\text{C}$ . According to the estimates, the cathode temperature could reach  $200\text{--}300^\circ\text{C}$ . The measured pressure in the electrolysis chamber was about 16 atm. and the measured pressure in the vacuum chamber (2) was  $3\cdot 10^{-3}$  Torr. The hydrogen flow through Ni membrane to vacuum chamber is:

$$Q = 1.3 \cdot (P - P_0) \cdot S,$$

where  $P_0 = 2 \cdot 10^{-3}$  Torr is the initial pressure,  $P = 3 \cdot 10^{-3}$  (Torr) is the measured final pressure,  $S = 5$  l/s is the pumping speed. So, pure hydrogen flow through Ni membrane is  $Q \approx 0.006$  Ncm<sup>3</sup>/s or about 21 Ncm<sup>3</sup>/h.

### 3 Discussion

From Fig. 3 it is follows that the electrolyte temperature after 50 minutes of the process reaches  $60^\circ\text{C}$ , at which the transformation of Na bicarbonate into soda ash begins:



Therefore, measurements of the spectral composition of the generated gas were carried out at temperatures below  $50^\circ\text{C}$ . Processing of the instrumental spectra curves shown in Fig. 5 allows conclusion that in our case the gas generated during electrolysis consists of  $\sim 94\%$  hydrogen (Fig. 5b). It has been taken into account that the sensitivity of the mass spectrometer for hydrogen is approximately two times lower than for air. The spectrum of the generated gas differs from the spectra of pure hydrogen released from a balloon (Fig. 5c) and initial one in vacuum chamber of GAS device by the noticeable increase of water ( $\approx 3\%$  vol.), oxygen and CO ( $\approx 1.5\%$  vol. each). These results are very different from the available literature data on water electrolysis (reaction equation  $2\text{H}_2\text{O} = 2\text{H}_2 + \text{O}_2$ :  $66\% \text{H}_2 + 34\% \text{O}_2$ ). To clarify the physicochemical reasons for this, additional investigations are necessary; which we are going to carry out in the nearest future. Here we primarily consider why such low values registered in the testing experiments on measuring the pure hydrogen flux through Ni diffusion-catalytic membrane.

One need to stress, that penetration of hydrogen through the wall of Ni cathode (membrane) is a complex process consisting of a number of sequential reactions: dissolution (absorption) in the metal, including hydrogen molecules dissociation and ionization, diffusion of atoms and ions in the metal volume, release to the surface of the back side of the membrane, hydrogen atoms recombination, desorption of hydrogen molecules. In contrast to  $\text{H}_2$  permeation from the gas phase, in the case of electrolysis, hydrogen will reach the membrane surface in various states:  $\text{H}_2^+$ ,  $\text{H}^+$ ,  $\text{H}$ . Ions, atoms and charged hydrogen molecules can easily overcome the potential barrier at the surface-metal interface. Therefore, the surface processes cannot be the limiting stage of the process in this case. Moreover, we expect that under such conditions the near-surface layer of the metal can be saturated with hydrogen to high concentrations. Diffusion in the volume of the metal, according to first Fick's law, is proportional to  $D(n_0 - n)/d$ , where  $n_0$  is the hydrogen concentration on the inlet side of the membrane,  $n$  is the one on the other side,  $D$  is the diffusion coefficient. Since in our case  $n_0 \gg n$ , and the thickness of the membrane is small ( $d = 0.2\text{mm}$ ), we can assume that in our case  $K \sim n/d \sim P^{0.5}/d$ , where  $K$  is the permeability coefficient,  $P$  is the hydrogen pressure on the inlet side of membranes. On the other hand,  $K = S \cdot D$ , where  $S$  is the solubility coefficient of hydrogen in nickel. Both coefficients depend exponentially on temperature, i.e.  $K = K_0 \cdot e^{-E/kT}$ , where  $E = E_d + E_s$  is the activation energy of hydrogen permeability ( $E_d$  is the activation energy of diffusion,  $E_s$  is the activation energy of solubility). It can be assumed that it is the temperature dependence of permeability that is the limiting factor. Indeed, according to literature data, to obtain significant hydrogen flows through metals, temperatures above  $350^\circ\text{C}$  are required [4]. So, in order to obtain essential hydrogen flows through Ni membrane it is necessary to increase its temperature, at least, up to  $400^\circ\text{C}$ .

### 4 Summary

We have designed, manufactured and tested the combined experimental installation, which allows not only studying the processes during electrolysis and the hydrogen permeability of diffusion-catalytic membranes (cathodes), but also research on the possibility of decomposition of water vapour and electrolysis products under the impact of plasma discharges.

The current-voltage characteristics of the electrolysis process and the spectra of the generated gas have been measured. It is shown that at temperature of  $\text{H}_2\text{O} + 1\% \text{NaHCO}_3$  electrolyte of  $45^\circ\text{C}$  and a pressure in the electrolysis chamber of 4 atm, the generated gas is 94% vol. consists of hydrogen, 3%  $\text{H}_2\text{O}$  and 1.5% each of CO and oxygen. These results appeared to be different from the available literature data on water electrolysis (reaction equation  $2\text{H}_2\text{O}=2\text{H}_2+\text{O}_2$ : 66%  $\text{H}_2+34\% \text{O}_2$ ). To clarify the physicochemical reasons for this, additional investigations are required; which are going to be performed by our team in the nearest future.

The diffusion flux of pure hydrogen through a nickel membrane (cathode) has been measured. It is shown that for the pressure in the electrolysis chamber of 16 atm. and electrolyte temperature of  $\sim 200\text{-}300^\circ\text{C}$ , a pure hydrogen flow  $Q \approx 0.006 \text{ Ncm}^3/\text{s}$  or  $21 \text{ Ncm}^3/\text{h}$  is achieved. To further increase the flow significantly, it is necessary to grow up the cathode temperature, at least, up to  $400^\circ\text{C}$ .

Further upgrade of the experimental device is planned within the next step in this research to reach the required parameters, in particular, improvement of electrolysis chamber in order to increase pressure and temperature parameters and, as sequence, to increase pure hydrogen flow through the Ni diffusion-catalytic membrane. For the same purpose it is planned to test other materials for producing of diffusion-catalytic membranes (cathodes) and anodes.

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#### Contribution of Individual Authors to the Creation of a Scientific Article:

Gennadiy Glazunov: Conceptualization, Methodology, Investigation, Writing&Editing.  
Aleksey Konotopskiy: Methodology, Investigation.  
Dmitriy Yelisieiev: Technical support for conducting experiment.  
Igor Garkusha: Project administration, data analysis, editing.  
Sergey Maznichenko: Technical support for the experiment.

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#### Conflict of Interest

The authors have no conflicts of interest to declare that are relevant to the content of this article.

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